



Low band gap amorphous silicon deposited under He dilution in the γ regime of an rf glow discharge: properties and stability

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Abstract

A new type of hydrogenated amorphous silicon film having variable bandgap (1.7–1.5 eV) has been developed in an rf powered plasma enhanced chemical vapor deposition system using a mixture of silane and helium at a substrate temperature of 210°C. The deposition conditions were chosen so that the rf glow discharge occurs in the γ regime, usually avoided because of powder formation. The influence of the chamber pressure, on the optical gap, the hydrogen content and the electronic properties is presented. Increasing the pressure up to 1.8 Torr is found to decrease the optical gap down to 1.5 eV. The densities of states of these films were measured by electron spin resonance, constant and modulated photocurrent techniques. The density of states above the Fermi level is found to be two orders of magnitude less than that of standard amorphous silicon. Moreover, unusually fast kinetics of degradation are observed. This new material could be a good alternative to amorphous silicon germanium alloys.

1. Introduction

Presently, amorphous silicon (a-Si:H) solar cell technology confronts obstacle from two major fronts: instability of single junction cells due to light-induced metastability of the intrinsic layer (Staebler–Wronski effect) and inadequate electrical performance of multijunction cells due to poor electronic properties, for instance low hole diffusion length, in the intrinsic material of the bottom cell, made of amorphous silicon germanium (a-SiGe:H) alloy [1]. A great deal of research has been devoted to the understanding and hence, control of light-induced metastability as well as searching for a-SiGe:H al-

loys having better electronic properties than the conventional one. However, after more than ten years of research, it is believed that both aspects are intrinsic properties of a-Si:H and a-SiGe:H alloys respectively. We now report electronic properties, defect densities and light-induced metastability of a new class of materials: low bandgap (1.7–1.5 eV) a-Si:H films prepared without any kind of alloying. As far as devices based on these materials are concerned, it is possible they will exhibit better efficiency for single junction as well as better initial electrical performance in multijunction a-Si solar cells.

2. Experimental details

The a-Si:H films have been deposited from a mixture of silane and helium by rf powered (13.56

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MHz) plasma enhanced chemical vapor deposition (PECVD, Anelva Corp. Japan) [2]. The substrate temperature T_s and rf power density during deposition were maintained at 210°C and 15 mW/cm² respectively. The chamber pressure P_r was varied from 0.5 to 2.2 Torr in a regime that is conventionally known as a powder regime and hence is usually avoided for deposition of device grade a-Si:H. For the deposition of all films the total flow of the silane and He mixture was maintained at 42.5 sccm. The optical gap of the films were estimated by transmission/reflection measurement and confirmed by the internal quantum efficiency of palladium/low band gap a-Si:H Schottky barrier solar cells. The mobility-lifetime products ($\eta\mu\tau$) have been measured under bandgap illumination and at a generation rate of $3 \times 10^{18} \text{ cm}^{-3} \text{ s}^{-1}$. The bonded hydrogen content (C_H) has been estimated from infrared vibrational spectroscopy. The density of states (DOS) of these materials has been investigated by complementary techniques such as electron spin resonance (ESR) and the constant photocurrent (CPM) and modulated photocurrent (MPC) experiments. The MPC experiment was performed at different temperatures ranging from 150 K to 390 K in 30 K steps and, at a given temperatures, with frequencies ranging from 12 Hz to 40 kHz. The reconstructed DOS from MPC data was estimated from equations presented elsewhere using the following parameters [3]: DOS at the band edge $N(E_c) = 10^{21} \text{ cm}^{-3} \text{ eV}^{-1}$, attempt to escape frequency $\nu = 10^{12} \text{ s}^{-1}$ and extended states mobility $\mu = 10 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. Light-soaking of the samples has been performed either under AM1.5 or under a flux of 400 mW cm^{-2} of a volume absorbed light ($\lambda > 640 \text{ nm}$).

3. Results

Fig. 1 shows the variations of the deposition rate (R_D), the optical gap and C_H of low gap a-Si:H films with P_r . It is observed from the figure that R_D sharply changes for P_r higher than 1.0 Torr. This is an indication that the plasma energy transfer mechanism during film growth changes from α to γ regime, usually avoided because of powder formation [4]. However, infrared analysis of the low bandgap a-Si:H, deposited with He dilution, shows

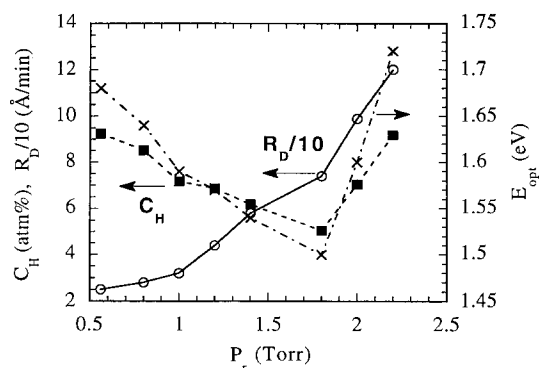


Fig. 1. Variations of deposition rate (R_D), optical gap (E_{opt}) and bonded hydrogen content (C_H) of a-Si:H with P_r . Lines are drawn as guides for the eye.

that the polyhydride $[(SiH_2)_n]$ bonds as well as bonded hydrogen content in these films systematically decrease with increasing chamber pressure for $P_r < 1.8$ Torr [5]. This indicates that with helium dilution of the silane, powders are not influencing the microstructure of the films while the presence of electronically excited He atoms (20 and 24 eV) rather indirectly improved it [5]. Consistent with the decrease of C_H the optical gap of the films systematically decreases with P_r : for instance the optical gap of a-Si:H films deposited with $P_r = 1.8$ Torr is 1.5 eV. These low values of optical gap are confirmed by the red response of Schottky barriers and pin solar cells based on these materials [6]. The X-ray diffraction analysis of these samples show peak characteristic of typical of amorphous silicon. Thus this new class of materials can be used as an alternative to a-SiGe:H alloys in multijunction solar cells.

Fig. 2 shows the variations of $\eta\mu\tau$, dark conductivity (σ_d) and photosensitivity (σ_{ph}/σ_d) of low bandgap a-Si:H with chamber pressure. In Fig. 1 it was shown that with increasing P_r the optical gap of the material decreases. Comparing Figs. 1 and 2 it may be noted that unlike the case for a-SiGe:H alloys, the $\eta\mu\tau$ products of low bandgap a-Si:H increase with decreasing optical gap (with P_r). Moreover, the values of $\eta\mu\tau$ and photosensitivity of a-Si:H having a gap of 1.5 eV are $5 \times 10^{-5} \text{ cm}^{-2} \text{ V}^{-1}$ and 7×10^4 respectively, much higher than the corresponding parameters of device grade a-SiGe:H alloys of the same band gap.

Test of light induced degradation is imperative

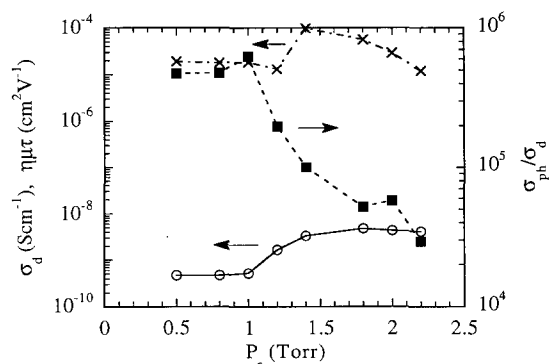


Fig. 2. Variations of the $\eta\mu\tau$, σ_D and photosensitivity (σ_{ph}/σ_D) with P_r . Lines are drawn as guides for the eye.

before any material is acceptable for a-Si:H cell application. Fig. 3 represents the variations of $\eta\mu\tau$ with light-soaking time under AM1.5 illumination at room temperature for all samples having different bandgaps (1.7–1.5 eV). It is surprising to note that the $\eta\mu\tau$ values of all the samples saturate within short time (20 h) and saturated values ($10^{-6} \text{ cm}^2 \text{ V}^{-1}$) are comparable to that of annealed standard a-Si:H films. It is also observed that E_F of the films has moved deeper in the gap by approximately 150 meV after saturation. In order to ensure that the saturation of $\eta\mu\tau$ is related to the bulk of the materials and not to any surface related effects, the kinetics of light-induced metastability of low bandgap

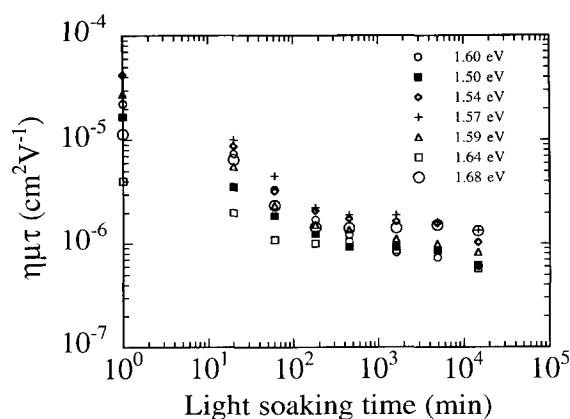


Fig. 3. Variations of the $\eta\mu\tau$ product of the a-Si:H samples having different gaps with light-soaking time under AM1.5 illumination at room temperature.

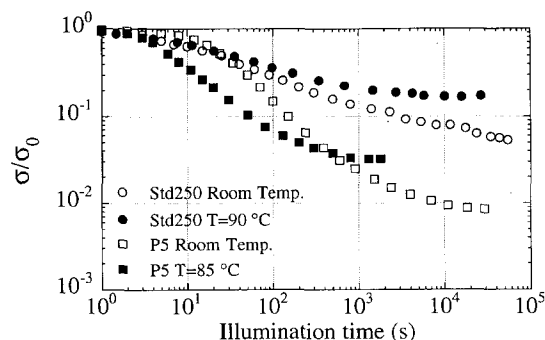


Fig. 4. Variations of normalized photoconductivity of standard (Std) and low gap (1.55 eV) samples with light-soaking time under 400 mW cm^{-2} illumination at room temperature and 85°C .

(1.60 eV) and standard a-Si:H film were compared under volume absorbed light at room temperature and at high temperature (85°C) with an illumination flux of 400 mW cm^{-2} . The results of the measurement are shown in Fig. 4. Both at room as well as at high temperature (85°C) the saturation time of photoconductivity for the low bandgap a-Si:H are much shorter than that of standard a-Si:H. For instance, at room temperature the low band gap sample reach saturation within 3 h whereas, in the same time the standard sample is only partially light-soaked (LS), since the complete saturation of the standard sample would have been reached only after a few days of continuous illumination.

In Fig. 5 the DOS (reconstructed from MPC data)

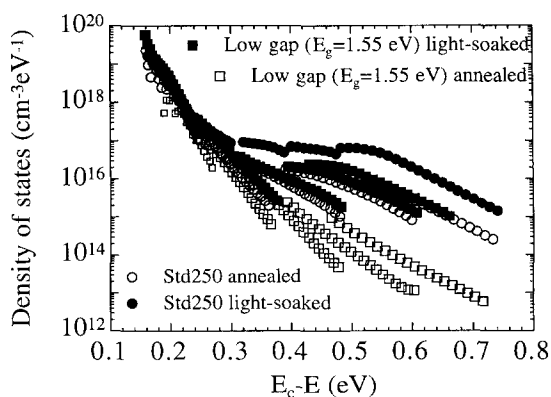


Fig. 5. DOS above the Fermi level reconstructed from MPC data of standard (Std) and low gap (1.55 eV) samples in their annealed (open symbols) and light-soaked states (full symbols).

of low bandgap (1.55 eV) a-Si:H films are compared with that of standard a-Si:H deposited without dilution in their annealed and LS states. The striking feature of the DOS above E_F of low bandgap a-Si:H in the annealed state is that it is two orders of magnitude lower than that of annealed standard a-Si:H, however according to the results from CPM both DOS below E_F are similar. In the LS state, the DOS above E_F of the low bandgap material is of the same order of magnitude to that of the DOS of the standard material in the annealed state.

4. Discussion

Although the films are deposited under the condition generally known as powder regime, the structural analysis by infrared spectroscopy indicates that with helium dilution of silane, the small particles in the plasma (powders) are not influencing the microstructure of the films while the presence of electronically excited He atoms (20 and 24 eV) rather indirectly improve a-Si network structure [5]. In previous section it has been noted that the normalized photoconductivity of low band gap samples are higher than that of conventional a-SiGe:H films having comparable optical gaps. From the dark conductivity activation energy measurement it has been observed that the position of the Fermi level (E_F) of all low bandgap a-Si:H films with respect to the conduction band varies between 0.75 and 0.65 eV for the highest and lowest band gap materials, which excludes the possibilities of auto-doping of films during deposition. Moreover, from ESR and CPM measurement it is noted that the deep defect densities of low bandgap a-Si:H films vary between 7 to $9 \times 10^{15} \text{ cm}^{-3}$ and that the width of the valence band tail states ranges from 50 to 59 meV. Thus dangling bond density and valence band tail width are comparable to that of device grade standard a-Si:H deposited without dilution at $T_s = 250^\circ\text{C}$; however they are lower than that of a-SiGe:H alloys having comparable optical gap. Thus the high values of photoconductivity of low band gap samples cannot be explained neither from the position of Fermi level nor from the measurement of deep defect density by ESR and CPM techniques. However it has been observed from MPC data that the DOS above

E_F systematically decreases with the increase of P_r if $P_r < 1.8$ Torr and it is one to two orders of magnitude less than that of standard a-Si:H film (Fig. 5). Thus high values of $\eta\mu\tau$ may be linked to the DOS above E_F of these films.

From Fig. 4 it is noted that the DOS of light soaked (LS) standard sample was obtained at room temperature after 10^5 s of illumination, that is before the complete saturation was reached whereas the DOS of the LS low gap sample was measured after full saturation. For the standard sample, after full saturation, the deep defect density would have been much higher than that presented here [7]. In spite of that, the DOS obtained for the standard sample in its partially LS state is higher than that of the LS low gap material. Since the DOS above E_F of the low gap sample in its LS state is comparable to that of the standard sample in its annealed states, one could expect to obtain the high values ($10^{-6} \text{ cm}^2 \text{ V}^{-1}$) of saturated of $\eta\mu\tau$ products of low band a-Si:H as described above. More experimental results are to be collected before any model of this completely different DOS above the Fermi level and kinetics of degradation of these samples can be given.

5. Conclusions

For the first time, low bandgap a-Si:H has been developed at $T_s = 210^\circ\text{C}$ in PECVD reactor exploiting an unexplored region of parameter space. The optoelectronic properties of these materials are superior to that of a-SiGe:H alloys having comparable bandgaps. The DOS above Fermi level and kinetics of light-induced degradation of these films are different from that of standard a-Si:H films. These properties raise the hope that this new class of materials can be a better alternative to a-SiGe:H alloys for multijunction and also for single junction solar cells.

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